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Per Dr. Donald Polk, ONR/Code 1131M

OFFICE OF NAVAL RESEARCH

FINAL REPORT

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1 MAY 81 -- 30 NOV 86

"RAMAN SPECTRA OF GLASSES"

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During the five years of the ONR contract first under Dr. Robert Pohanka, and then later under Dr. Donald Polk, we carried out Raman studies of glasses which resulted in 14 publications within the 1 May 81 to 30 Nov 86 period. Furthermore, three other publications during 1987-1988, that is, outside of the contract period, arose directly from the contract work, or were the culmination of it.

The 17 total publications are listed chronologically at the end of this report. Note that the 3 later publications are Refs. (15, 16, and 17). These three references involve Raman spectra of molten silica (SiO_2) at 2050 °C (17), Raman spectra, plus a theoretical treatment of the data, for complex fluorozirconate anions in ZBLAN glasses and melts (16), and, infrared studies of hydrogen-bonding on the surface of wetted BeF_2 glass (15).

The Raman work during the 81-86 contract period involved B_2O_3 glasses and melts (9, 10), optical fiber work on SiO_2 involving high tensile stress and high torsional forces (3, 4, 5, 7, 8, and 11), reversibly and irreversibly compacted fused silica (1, 7), ZrF_4 -based glasses and melts (13, 16), BeF_2 glass (15), silica aerogel (12), heat-treated silica aerogel (14), silica

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→ glass (6), overtone spectra from OH in silica glass (2), and molten silica (17). We will begin by describing the ⁷B₂O₃ Raman work. borates, zirconium fluorides, beryllium fluoride. (mgm) ←

The Raman work on vitreous and molten B₂O₃ involved the Raman shift region of 0 to 900 wavenumbers at temperatures from 4 K to about 1880 K, and at pressures to 8 kbar (9, 10). The main emphasis of this work was on the low-frequency Raman region, with particular attention to a Raman band which, at room temperature, occurs near 24 cm⁻¹. Large changes in the position of this nominal 24 cm⁻¹ band were observed in the temperature and pressure ranges studied.

We observed that the peak position of the 24 wavenumber band, when corrected for the Bose-Einstein thermal population factor, decreased significantly, and in a sigmoid manner with temperature rise from room temperature to 1880 K. A very large drop in the frequency of this band occurred at the glass transition temperature, T_g. We also observed that the Bose-Einstein corrected peak frequency was linear in the bulk modulus, over a temperature range of 600 degrees. This indicated that the 24 wavenumber feature is a collective mode involving large assemblies of cages and/or rings in the glass. We later observed the same general type of behavior for a low-frequency collective mode in ZrF₄-based glasses and melts (13), that is, the sigmoid frequency-temperature behavior, with the largest change in frequency at T_g.

A long-term project which was initiated under the aegis of Dr. Robert Pohanka involved obtaining Raman spectra from silica

glass (6), and especially from molten SiO_2 at 2000 °C, and above (17). Raman spectra from molten silica are exceptionally difficult to obtain, obviously, and we experienced severe difficulties with the molten silica reacting strongly with crucible materials, and with the extremely intense thermal radiation. However, we have now succeeded in obtaining Raman spectra of molten silica at 2050 °C, which is well above the melting point! We did this by side-stepping the problems, that is, we went to other methods.

We employed 10.6 μm CO_2 laser heating to make a molten puddle of SiO_2 in the center of a large piece of silica. We used a co-axial 532 nm Nd-YAG laser beam for excitation of the Raman spectra. For detection, we used a gated, intensified, array detector to collect signals in real time. This detector was synchronized with the 10 nsec laser pulse. Effective rejection of the blackbody emission from the weaker Raman scattering was thus achieved.

We decided to perform the Raman work with molten silica at the Battelle Pacific Northwest laboratory in cooperation with Dr. Gregory J. Exarhos. We did this, because we did not have the specific facilities to perform this extremely high temperature Raman work at Howard university. Of course, we do have very extensive facilities at Howard University for CW laser-Raman spectroscopy of melts to about 1600 or 1800 °C. We have four complete laser-Raman instruments; three holographic grating double-monochromators, and one holographic triple-monochromator, plus the required argon-ion lasers.

The Raman results from molten silica at 2050 °C indicated that the six and eight membered ring modes persist at the high temperatures of the melt. Also a gradual break-up of the low temperature 3-dimensional glass structure into rings and chains is indicated at high temperatures. In particular, the pulsed-excitation, gated detection method was clearly found to be effective in obtaining Raman spectra from incandescent materials at very high temperatures.

The Raman results from ZrF₄-based glasses over a series of stoichiometric F/Zr mole ratios from 4.6 to 8 indicated that a series of fluorozirconate anions exist in these glasses (13, 16). In this work we studied the change in the Raman peak position, (in wavenumbers) for the totally symmetric breathing mode of the series of complex anionic species (16). This symmetric breathing frequency decreases non-linearly with increase of the stoichiometric F/Zr mole ratio from 4.6 to 8.0.

We developed a first-order theoretical treatment in which the frequency (in wavenumbers) was shown to be a non-monotonic cubic function (no quadratic term) of the equilibrium Zr-F distance. We used Zr-F distances taken from x-ray results for coordination numbers from 4 to 8. Our theory explained the shape of the frequency versus Zr-F distance (nonmonotonic cubic dependence) satisfactorily. Moreover, our theory clearly indicated that bridging effects between anions are very weak, or absent, in the melts, as also indicated previously by workers at the Oak Ridge National Laboratory.

The work with BeF₂ glass (15) involved a quantitative

infrared investigation of the hydrogen-bonding on the wetted surface. We found that Be-OH groups are formed on the surface, but that these groups are extremely strongly hydrogen-bonded to a hydrated $\text{H}_3\text{O}^+ \cdots \text{F}^-$ complex. The $\text{H}_3\text{O}^+ \cdots \text{F}^-$ complex is itself a very strong one, for example, the strength of this complex is now the accepted explanation for the unusual weakness of HF in water. This hydronium-cation-fluoride-anion complex was never invoked previously in understanding the wetted BeF_2 surface, but its presence was absolutely essential in our quantitative explanation of the infrared data.

When a wetted BeF_2 surface is put into a high vacuum, the infrared absorbance near 3200 wavenumbers decreases slowly, and nonlinearly with time for several hundred hours. This indicates that it is the H_2O in the hydration sphere of the hydronium in the hydronium-fluoride complex that is lost in a series of stages. With this insight, we were able to make a quantitative interpretation of the nonlinear dependence of the absorbance versus pumping time. The first H_2O molecule is easier to remove from the complex than the second one, and so on. Accordingly, the absorbance versus time plot shows upward concavity, indicating that the first H_2O molecules come off faster than the following ones.

We also published a number of Raman articles dealing with the structure of silica glass (2, 3, 4, 5, 6, 7, 8, 11). The Raman measurements involved high tensile stress (7), reversible compression (7), irreversible compaction (1), high torsional forces (8), effects of tensile stress on OH absorption (11), and

OH overtones from SiO_2 (2). In addition we conducted studies of aerogel (12), and of heat-treated aerogel (14) to aid in our understanding of the silica structure.

The culmination of all of these studies on silica glass indicated that the central force and random-network models of vitreous silica are inadequate. Our data, in contrast, indicated that a correlated bond model is required, that is, one in which there is some correlation between the Si-O-Si bridging angle, the dihedral angle, and the Si-O bond distances in the silica glass (3, 4, 5, 7, 8, 14).

PUBLICATIONS IN THE 1981-1986 CONTRACT PERIOD

1. J. Chem. Phys. 74, 5328 (1981). (Pressure compacted silica)
2. J. Chem. Phys. 76, 1712 (1982). (OH overtones, silica)
3. J. Noncrystalline Solids 54, 323 (1982). (Interpretation, silica structure)
4. Proceedings of the International Conference on Glasses at Cambridge, England, 1982. (Interpretation, silica structure)
5. Proceedings of the International Conference on Glasses at Montpellier, France, 1982. (Interpretation, silica structure)
6. Applied Optics 21, 359 (1982). (Computer deconvolution of Raman bands from vitreous silica)
7. Chapter in "structure and Bonding in Noncrystalline Solids", G. E. Walrafen and A. G. Revesz, editors, Plenum, NY, 1983. (Correlation between parameters in the structure of silica)
8. J. Chem. Phys. 78, 5273 (1983). (Silica fibers, high torsion)
9. J. Chem. Phys. 79, 3609 (1983). (B_2O_3 glass and melt)
10. J. Chem. Phys. 80, 3807 (1984). (B_2O_3 glass, high pressure)
11. J. Lightwave Techn. LT-2, 646 (1984). (Effects of tensile stress on OH-uptake)
12. J. Chem. Phys. 82, 2472 (1985). (Aerogel, Raman)
13. J. Chem. Phys. 83, 4427 (1985). (ZrF_4 -based glasses)
14. J. Chem. Phys. 85, 771 (1986). (Thermal treatment, aerogel)

PUBLICATIONS BEYOND THE 1981-1986 CONTRACT PERIOD

15. J. Chem. Phys. 86, 6516 (1987). (OH on surface, BeF_2 glass)
16. SPIE, Vol. 929, Infrared Optical Materials, VI(1988)/133.

(ZrF₄-based ZBLAN glasses)

17. ICORS (International Conference on Raman Spectroscopy)

Proceedings, London, England. Conference 5-9 Sep 88.

(Molten silica, Raman spectra)

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